Organometallics 1987, 6, 2270–2271

In conclusion, neutralization of FeCH$_x^+$ ($x = 0$–3) species generates neutral analogues FeCH$_x$ ($x = 0$–3), having lifetimes $t \geq 10^{-5}$ s. No evidence is available for the involvement of hydridometal species, for $x = 2$ or 3.

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Silacarbonyl and Silathiocarbonyl Ylides

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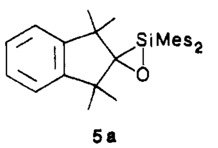
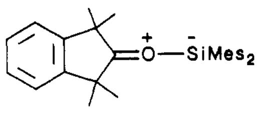
Summary: The silacarbonyl ylide **4a** has been observed by the photolysis of oxasilirane **5a** in an isopentane/3-methylpentane matrix at 77 K. The ylide was also generated independently by the direct reaction of dimesitylsilylene with tetramethyl-2-indanone. The silacarbonyl ylide is intensely blue in color with a maximum at 610 nm. Excitation of this band with visible light resulted in the formation of oxasilirane **5a**. A silathiocarbonyl ylide has also been generated by either photolysis of a thiasilirane or the direct reaction of silylenes with indanethione.

The formation and characterization of carbonyl ylides in the photochemical ring opening of aryloxiranes[1] or in the reaction of carbenes with ketones[2] have been well-established by low-temperature photolysis or flash laser photolysis. However, the chemistry of silacarbonyl ylides, the silicon analogues of carbonyl ylides, is completely unknown. Recently we reported synthesis of oxasilirane **5a**[3] and thiasilirane **5b**[4] and the photochemical fragmentation of **5a** to a silylene and a ketone in solution, probably, via a silacarbonyl ylide intermediate.[5] We report here the first spectroscopic evidence for the intermediacy of the hitherto unknown silacarbonyl and silathiocarbonyl ylides in a low temperature matrix.



5a



4a (λ_{max} = 610 nm)

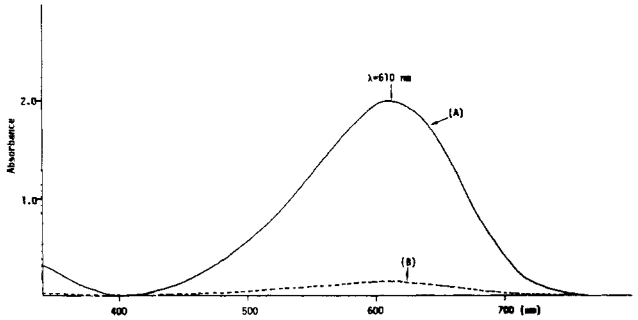


Figure 1. (A) After photolysis of **5a** with a low-pressure mercury lamp (254 nm) for 10 min in IP/3-MP (6:4) at 77 K (—). (B) After the additional irradiation of the above sample for 5 s with a xenon lamp ($\lambda > 460$ nm) (- - -). The band completely disappeared by 60-s irradiation with $\lambda > 460$ nm.

Irradiation of oxasilirane **5a** (0.02 mmol) in an isopentane (IP)/3-methylpentane (3-MP) matrix[6] at 77 K with a low-pressure mercury lamp led to the appearance of a new band at 610 nm in the UV–vis spectrum, and the matrix became intensely blue in color (Figure 1). This absorption band was stable at 77 K on prolonged standing. However, it immediately disappeared on brief irradiation with a xenon lamp ($\lambda > 460$nm) or when the matrix was allowed to melt. These results appear to be related to the photochemistry of aryloxiranes in rigid organic glasses to give colored intermediates that can be eradicated either by irradiation into the visible absorption band or by warming the matrix.[1] The colored species was also observable at 610 nm in the photolysis of **5a** in 3-MP glass at 77 K.[7]

This colored species was independently generated by the reaction of dimesitylsilylene (**2**) with 1,1,3,3-tetramethyl-2-indanone (**3a**). Thus, irradiation of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**1**) in the presence of **3a** in IP/3MP at 77 K with a low-pressure mercury lamp produced a colored species with λ_{max} at 573 nm due to dimesitylsilylene (**2**).[8] The absorption bands at 610 and 420 nm increased in intensity in the dark at the almost same rate as the decrease of the band at 573 nm, showing that **2** reacts with **3a** or dimerizes to tetramesityldisilene (420 nm) in the matrix at 77 K (Figure 2).[9] Irradiation of the red solution of the 610-nm species, with a wavelength of light greater than 460 nm, or melting the matrix resulted in production of the oxasilirane **5a**.[10]

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[1] (a) Trozzolo, A. M.; Leslide, T. M.; Sarpotdar, A. S.; Small, R. D.; Ferraudi, G. J. *Pure Appl. Chem.* **1979**, *51*, 261. (b) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 5639. (c) Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2818. (d) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (e) McGimpsey, W. G.; Scaiano, J. C. *Tetrahedron Lett.* **1986**, *27*, 547. (f) Franco, P. G. *Rev. Chem. Intermed.* **1986**, *7*, 155. (g) Ibata, T.; Liu, M. T. H.; Toyoda, J. *Tetrahedron Lett.* **1986**, *27*, 4383.

[2] (a) Wong, P. C.; Griller, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5106. (b) Bekhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289. (c) Prakash, G. K. S.; Ellis, R. W.; Felberg, J. D.; Olah, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1341.

[3] Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1982**, *23*, 5323.

[4] Ando, W.; Hamada, Y.; Sekiguchi, A.; Ueno, K. *Tetrahedron Lett.* **1983**, *24*, 4033.

[5] Ando, W.; Hamada, Y.; Sekiguchi, A. *J. Chem. Soc., Chem. Commun.* **1983**, 952.

[6] The IP/3-MP matrix is a relatively soft matrix compared to the 3-MP matrix. The viscosities of the matrices at 77 K are as follows: IP/3-MP (6:4), 1.8×10^8 P; 3-MP, 9.4×10^{11} P. Lambardi, J. R.; Raymonda, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964**, *40*, 1148.

[7] The band at 564 nm gradually shifted to 610 nm without annealing when the matrix was allowed to stand at 77 K in the dark (ca. 5 h). The change of the conformation of **4a** will result in a bathochromic shift due to electronic reasons. In a soft matrix, the most stable conformation will be readily achieved.

[8] The bands at 573 and 420 nm are due to dimesitylsilylene (**2**) and tetramesityldisilene, respectively. In 3-MP matrix, the bands of **2** appeared at 577 nm. West, R.; Fink, M. J.; Michel, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R. *Silicon, Germanium, Tin Lead Compds.* **1986**, *1*, 75–80. The small hypsochromic shift to **2** from the 3-MP matrix to the IP/3-MP matrix is probably due to solvent effects.

[9] Dimesitylsilylene can dimerize to tetramesityldisilene at 77 K in a soft matrix without annealing the matrix. Sekiguchi, A.; Hagiwara, K.; Ando, W. *Chem. Lett.* **1987**, 209.

[10] The products **5a** and **5b** were identified by comparison of their spectra with those of authentic samples.

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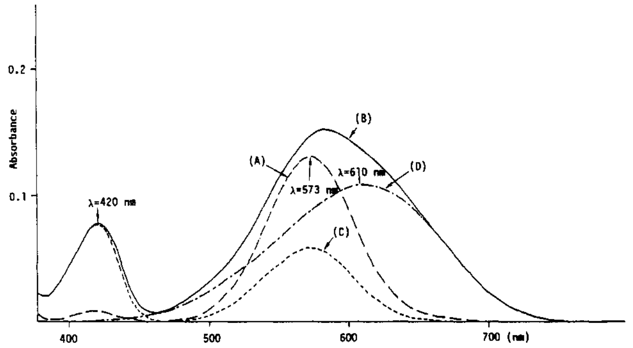
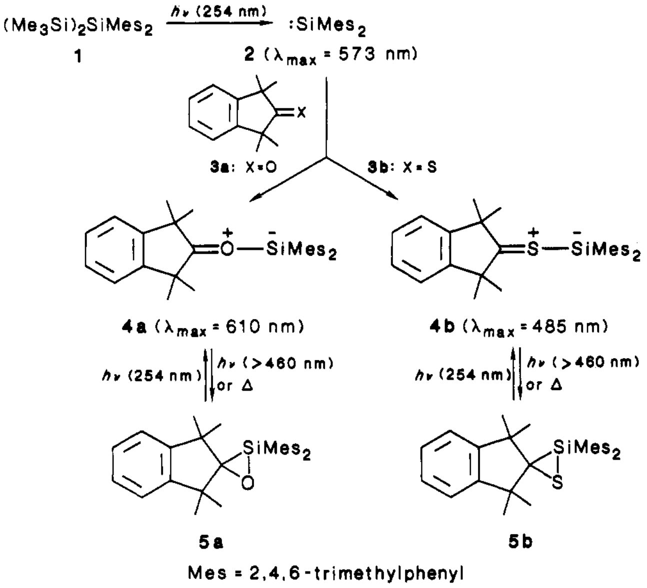


Figure 2. (A) After photolysis of 1 (0.023 mmol) with a low-pressure mercury lamp (254 nm) for 20 min in the presence of **3a** (0.06 mmol) in IP/3-MP (6:4) at 77 K (---). (B) The above sample was allowed to stand in the dark at 77 K for 3 h (—). The absorption band B is composed of band D due to **4a** and band C due to **2**. (C) After irradiation of the above sample for 1 min with a wavelength of light greater than 460 nm (···).

Scheme I

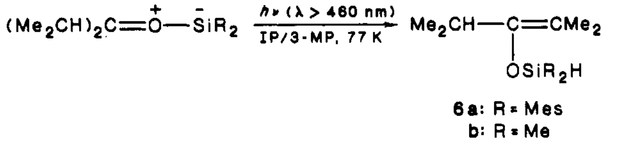


When a similar photolysis of 1 in the presence of **3a** was carried out in 3-MP at 77 K, initially only a band with λ_{max} at 577 nm due to **2**[8] was observed. After careful annealing of the matrix and recooling, this band diminished and new bands were formed with λ_{max} at 610 and 420 nm. This shows that the dimesitylsilylene (**2**) reacted with **3a** to give a species with λ_{max} at 610 nm or dimerized to tetramesityldisilene (λ_{max} = 420 nm). On the basis of these results, it is a quite reasonable to assume that the colored intermediate is most probably silacarbonyl ylide **4a** (Scheme I).

An ESR examination of silacarbonyl ylide **4a** was carried out in the IP/3-MP matrix at 77 K, but no signal was observed. This indicates that the ground state of **4a** is a singlet and the silacarbonyl ylide should be a zwitterionic structure rather than diradical. Excitation of **4a** with visible light may lead to the diradical which readily undergoes ring closure to give **5a**.

Reaction of dimesitylsilylene (**2**) with diisopropyl ketone in IP/3-MP at 77 K gives a species with λ_{max} at 582 nm. This band was eradicated by warming or by irradiation with light of wavelength greater than 460 nm with concurrent formation of a silyl enol ether **6a** via α-hydrogen abstraction of the silacarbonyl ylide.[11]

Photolysis of dodecamethylcyclohexasilane in the presence of diisopropyl ketone in IP/3MP at 77 K again produces a band at 625 nm. The band immediately disappeared on excitation to give a silyl enol ether **6b**.[12]



Silathiocarbonyl ylide **4b** was observed in the photolysis of thiasilirane **5b**. Thus, photolysis of **5b** in IP/3-MP at 77 K showed a band at 485 nm due to the silathiocarbonyl ylide **4b** which has a significant lifetime at 77 K but which immediately disappeared either on melting the matrix or on a 460-nm irradiation. The results are in contrast to the photochemical behavior of thiiranes in the carbon system.[13]

The reaction of **2** with tetramethylindanethione (**3b**) in IP/3MP at 77 K again produces a band at 485 nm, assigned to the silathiocarbonyl ylide. Upon excitation of this band, the thiasilirane **5b** was isolated as the sole product (Scheme I).[10] Experiments are in progress to further elucidate the mechanism and generality of this reaction.

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(11) Compound **6a**: NMR (CCl_4, δ) 0.83 (d, 6 H, *J* = 7 Hz), 1.52 (s, 3 H), 1.63 (s, 3 H), 2.23 (s, 6 H), 2.37 (s, 12 H), 2.76 (hept, 1 H, *J* = 7 Hz), 5.88 (s, 1 H), 6.65 (s, 4 H); MS, *m/e* 380 (M^+).

(12) Compound **6b**: NMR ($CDCl_3$, δ) 0.27 (d, 6 H, *J* = 3 Hz), 0.97 (d, 6 H, *J* = 7 Hz), 2.63 (br s, 6 H), 3.80 (hept, 1 H, *J* = 7 Hz), 5.82 (hept, 1 H, *J* = 3 Hz); MS, *m/e* 172 (M^+).

(13) Griffin, G. W.; Bertoniere, N. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. 1, pp 333–334.